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THE REACTIONS PERTAINING TO ZINC-SILVER AND CADMIUM-SILVER BATTERIES

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ABSTRACT

The Zn(II) precipitate formed with KOH appears to contain about 15-20% $Zn(OH)_2$, the remainder being ZnO. Considerable NH_3 is coprecipitated, possibly as $Zn(NH_3)_4^{2+}$, when Zn(II) is added to NH_3 solution. While the NH_3 itself does not appear to be tritiated, the effect is to inhibit the formation of tritiated hydroxide.

Significant loss of tritium through exchange with water was observed during extensive washing. The loss can be virtually eliminated by washing with tritiated water. The procedure does not produce an abnormally high activity in the precipitate if it is carefully dried before counting.

AgO is converted almost completely to Ag_2O in less than 12 hours at 140^oC. The diffusion of oxygen from the interior of the material during decomposition may be slow and the AgO on the surface may be more active than that in the interior.

Electrochemically-prepared AgO appears to exist in a fairly unstable state initially, but changes to a more stable form within 2-4 weeks after being prepared.

OBJECTIVES

The objectives of the contract are three-fold:

(1) The characterization of cadmium and zinc anodic reaction products.

(2) The thermal decomposition of silver oxide and the measurement of the rate of decomposition of AgO and Ag_2O at various temperatures between 110° and 200°C.

(3) The deposition of silver cathode material on zinc anodes.

This report deals with parts of the first two objectives and will be divided into: (A) the investigation of the precipitates of Zn(II) and Cd(II) formed by precipitation with alkaline solutions and (B) thermogravimetric investigations of AgO. Preliminary experimentation on part (3) will begin next quarter.

A. PRECIPITATION OF ZINC AND CADMIUM OXIDES

Introduction

While the results shown in the previous report (1) suggested that ZnO was the predominant species formed by precipitation with KOH and $Zn(OH)_2$ was the predominant species formed by precipitation with NH_3, several disturbing observations remained unexplained and certain pertinent questions unanswered. In all cases where precipitation of Zn(II) was accomplished with KOH, the tritium activity remaining in the precipitate suggested that only a small amount of $Zn(OH)_2$ was formed. The conclusion was based on the assumption that the only tritium remaining was bonded to the zinc as the hydroxide. However, the apparent amounts of $Zn(OH)_2$ ranged from 2.2 to 12.1% (1) with disturbing standard deviations within each set of data. Furthermore, there was definite

evidence of significant exchange of tritium between the precipitate and water with the possibility that washing seriously reduced the activity of the solid thus leading to an erroneous conclusion that little $Zn(OH)_2$ was present. Two ways in which tritium might be washed out of the precipitate are represented by the following equations:

$$Zn(O^3H)_{2(s)} + H_2O = Zn(OH)_{2(s)} + {}^3H_2O \quad (1)$$

$$Zn(O^3H)_{2(s)} = ZnO_{(s)} + {}^3H_2O \quad (2)$$

Equation (1) represents an exchange while equation (2) represents a dehydration. The latter is less likely to be reversible than the former.

In NH_3 precipitations, where relatively large amounts of $Zn(OH)_2$ apparently formed, there was the possibility that tritiated NH_3 was formed and was bonded to the zinc so that what appeared to be zinc hydroxide was actually an ammine complex. This did not seem likely, but could not be discounted as a possibility.

Several experiments were proposed to try to determine the effects of the washing procedures: (a) Precipitates were to be washed with water and washings analyzed for tritium at each step in the procedure. (b) The washing procedure was to be changed to make each washing more effective. (c) The precipitates were to be washed with ${}^3H_2O$ to inhibit reaction (1) if it occurs. Some of these experiments are described below.

Experimental

Procedures for preparation and analysis of materials have been described in the earlier reports (1,2).

Cadmium was precipitated with KOH and with NH_3 at $25^o \pm 0.2^oC$. Zinc was precipitated with KOH and with NH_3 at $25^o \pm 0.2^oC$, at $55^o \pm 0.5^oC$,

and without temperature control. The time required for each precipitation depended on the temperature, longer times being needed at 25^{o} than at 55^{o}. When temperature was not controlled, precipitation was performed rapidly.

Precipitates were washed in three ways and the extent of washing was varied. Until recently, each washing was done by adding 10-15 ml. of water to the precipitate, stirring the mixture with a glass rod, allowing it to settle, and decanting the supernatant through a filter funnel. From five to fifteen washings were performed on a sample. The process was slow and separation of each washing from the precipitate was incomplete. The current technique is to transfer the precipitate to a centrifuge tube, add 15 ml. of water, stir with a glass rod, centrifuge, and repeat the stirring and centrifugation. After the third centrifugation, the supernatant is decanted through a filter funnel. The whole procedure is repeated until washing is considered complete. This procedure is faster than the previous one and should provide close approach to equilibrium between the wash solution and the precipitate mixture.

The current procedure was modified in two experiments by adding sufficient $^{3}H_2O$ to the wash water to make its activity correspond to that in the supernatant at the end of the precipitation reaction. In this way, exchange of tritium in the precipitate with that in the wash water should be minimized. The precipitates washed by this modified procedure were dried in vacuum over P_2O_5.

The tritium activity in the washings was measured in 50-λ samples.

An inactive sample of zinc precipitate was formed by adding Zn(II) solution to concentrated NH_3. The precipitate was washed by the centrifuge method and the washings tested for NH_3 with Nessler reagent (3).

Results and Discussion

The results of the precipitations of Zn(II) with KOH are shown in Table 1. Each experiment comprises a single precipitation; groups of replicate experiments are separated by short lines in the middle of the table. In all cases, precision was poor, but some were much worse than others. The worst precision occurred where the washing was most complete. Thus, the average deviation from the mean for experiments (6-8) is 60%, that for experiments (1-3) is 23%, and that for experiments (9-11) is 13%. The precipitates in the last were probably more thoroughly washed than the others since the centrifuge method was employed. On the other hand, the wash water used for the last experiments contained ^3H_2O which inhibited exchange. This is strong evidence that extensive washing permits sufficient exchange between the tritiated solid hydroxide and the wash water to cause considerable error in the apparent hydroxide content of the solid. Still, one is reluctant to rely on incomplete washing since it may produce other errors just as serious. The use of ^3H_2O in the wash is feasible, but the time required for drying is considerable.

The results of the precipitation of Zn(II) with NH_3 are shown in Table 2. Here are seen the effects of more or less thorough washing on the activity in the wash water, the apparent $Zn(OH)_2$ content, and the precision of the results. The effect of changing the order of addition of reagents is also apparent.

Experiments (1-3) and (7-9) were identical except for the washing procedure and its extent. The first group, with less washing, shows a higher apparent hydroxide content and an average deviation from the mean of 46%, as compared to 60% for the second group. Experiments (4-6) and (10-12) were performed with quite different procedures yet

the results are more nearly the same and the average deviations from the mean are 2% and 6%, respectively. The latter group probably gave good results because the ^3H_2O in the wash inhibited exchange of tritium. It is interesting that more zinc was recovered in experiments (10-12) than in any of the others reported here. Experiments (1-6) were plagued with the difficulties of working in a system free of CO_2, thus losses are to be expected. Low results in experiments (7-9) may be caused by the very extensive washing.

The high activity in the last washings in experiments (7-9) are remarkable and have not been explained. The washings showed a high enough count throughout the series to suggest that more activity had been washed out than was originally present. Even more suprising is that the twelfth washing in each of these cases showed considerably higher activity than did the redissolved precipitates. Since the only source of tritium, presumably, was the precipitate being washed, this is difficult to understand. This phenomenon will not be investigated further for the present.

The results of experiments (4-6) where almost 100% $Zn(OH)_2$ is indicated, are particularly interesting. Results shown in Table 2 of the previous report (1) indicated that precipitates formed with NH_3 had rather high $Zn(OH)_2$ content and deviations between results were fairly low compared with those obtained more recently. The data shown in Table 2 of the present report were suprising; experimental similarities were sought. All of the experiments in Table 2, except (4-6), were performed by adding Zn(II) to the concentrated NH_3 solution. Exposure of the NH_3 solution to the atmosphere in a buret over the long period required for precipitation at controlled temperatures was considered

undesirable because NH_3 might be lost through evaporation or the solution might be contaminated with CO_2. Therefore, Zn(II) was added to the NH_3 solution---just the reverse of the procedure in all of the experiments reported previously. However, this method was found to be impossible at 55^o because the vapor pressure of the NH_3 was too great; therefore, NH_3 was added to Zn(II) at this temperature only. The results can be seen. The only similarity between the method used for experiments (4-6) and those reported previously is the addition of NH_3 to the Zn(II); almost every other aspect was different.

One might expect NH_3 to be strongly coprecipitated by $Zn(OH)_2$ or even ZnO if the NH_3 were in excess as is the case throughout most of precipitation when Zn(II) is added to NH_3. If $Zn(NH_3)_4^{2+}$ were formed, adsorbed on the precipitate and then occluded as more precipitate formed, the precipitate would contain less $Zn(OH)_2$ than expected even though all of the zinc were carried down. On washing, some of the ammine complex would be destroyed and it might be replaced by $Zn(OH)_2$ formed in the absence of tritium. In either case, the apparent hydroxide content would be low and be subject to the vagaries of the washing procedure. On the other hand, coprecipitation of NH_3 should be less if the NH_3 were added to the Zn(II) solution because the pH would never be high enough for complex formation and NH_3 would never be in excess except locally and briefly. Thus, the precipitate would be predominantly $Zn(OH)_2$ and ZnO and the hydroxide would be tritiated. This argument can account for the fact that there is a high apparent hydroxide content when the precipitate is washed with tritiated water even though the NH_3 was allowed to be in excess during the precipitation.

That NH_3, in some form, adheres strongly to the precipitate has been demonstrated by an experiment in which the precipitate formed with

NH_3 was washed until the washings showed no indication of ammonia. The precipitate was formed by adding Zn(II) to NH_3; the washing was done by the centrifuge technique. Only in the 14th washing had all indication of NH_3 disappeared.

Table 3 shows the results of precipitating Cd(II) with KOH and with NH_3 at $25^{\circ} \pm 0.2^{\circ}C$. The experiment with NH_3 was not satisfactory because losses through complex formation were severe; this phase of the work will not be continued. The precision of the KOH precipitations is not satisfactory, but the techniques developed with the zinc system may be applicable.

Conclusions

The data suggest, again, that ZnO is the predominant species formed when zinc is precipitated with KOH; however, the relative amount of $Zn(OH)_2$ is probably greater than was previously thought, being between 15 and 20%. $Zn(OH)_2$ is still considered the predominant species when zinc is precipitated by ammonia. The apparent hydroxide content depends on the procedure used for precipitation. Addition of ammonia to the zinc solution produces more reproducible results than addition of zinc solution to ammonia. Coprecipitation of the zinc ammine complex may actually prevent precipitation of some of the hydroxide from the tritiated solution so that the apparent hydroxide content is lower when ammonia is allowed to be in excess.

Cadmium precipitates show about 40% hydroxide. The results are sketchy, as yet, and more experiments of the type performed with the zinc system are necessary. Precipitation with ammonia is not practical at present and will be discontinued.

Proposed Work

The effect of adding ammonia to Zn(II) solutions is being

investigated at present. Washing is being done with tritiated water. Preliminary experiments to determine the form of the anodic products at porous zinc electrodes in KOH electrolyte solutions will begin and will probably form the major effort in future work on the zinc system.

The investigation of the cadmium precipitate will be continued and, if possible, some experiments with electrochemical oxidation will be started.

B. THERMAL DECOMPOSITION OF AgO

Experimental

AgO was prepared electrolytically according to a method described by Jolly (4). One sample was prepared using Pt-foil electrodes and another using Pt-grid electrodes. Thermograms were obtained as previously described (1) except that, for constant-temperature experiments, the thermocouple was mounted outside the hangdown tube and inside the furnace at a position close to the sample. Even with this modification, recorder noise was encountered after several hours. Further equipment modifications are being considered.

Results and Discussion

Electrochemically prepared AgO was initially black and rather crystalline as opposed to the dark gray powder formed chemically. However, the black color changed to the more characteristic gray after standing in the dark for a week or two. Unfortunately, no thermograms were made of the material shortly after preparation, so no comparison of thermal characteristics is available at present. Figure 1 shows a thermogram of the material prepared with Pt-foil electrodes. The form is much like previous thermograms. The midpoint of the second plateau occurs at about 0.51 which suggest that the samples contain a volatile impurity which does not show up at the heating rate employed. The

total weight loss for pure AgO on heating should be 12.91% of the original sample weight; the loss for this material was 13.30%. A small amount of moisture, for example, could account for this difference and for the upward shift in the plateau of the thermogram. Alternatively, a small amount of Ag_2O_3, which might not show in the thermogram, could also account for the shift.

Figure 2 shows a typical constant-temperature thermogram of chemically prepared AgO at 140°C. The results are normalized so that a maximum weight-loss would be represented as 1.000. The weight-loss at 11.6 hours of heating is 48.5% of the expected total if the material had been reduced to the metal. The loss corresponds to about 97% conversion of the AgO to Ag_2O. Oxygen is assumed to be the only substance lost, although this is not certain at this time. The maximum weight-loss found previously for this material was 13.19% of the original sample weight.

There is a curious "wobble" in the curve in Figure 2 early in the heating period. The initial rate of change is comparatively high, decreases slightly, then increases and continues to follow what might be called an "expected curve". This rate change has been observed in all constant-temperature thermograms of this batch where the temperature control was adequate. (It was not observed in the curve shown in the last report because the temperature was not well controlled in the initial stages of the experiment.) The phenomenon might be caused by some higher oxidation state of silver or by the presence of moisture. The latter seems less likely because one would expect water to be removed in less than a half hour.

Possibly a more attractive speculation is that oxygen from the surface layers is readily removed as soon as it is formed while oxygen

in the body of the material must have time to diffuse to the surface before it can escape. Thus, there would be a rapid, initial loss of weight which would slow as the surface layer became depleted. Then, as oxygen diffusing from the interior reached the surface, it would be lost and the rate would increase until an equilibrium between the rate of formation within the solid and the rate of removal from the surface was obtained. If this hypothesis is correct, the effect should be magnified at some other temperature; it is unlikely that diffusion rate and decomposition rate would change in exactly the same way with temperature. One might expect a similar observation in a varying-temperature thermogram if the heating rate were changed.

Conclusions

It is evident that AgO is converted almost completely to Ag_2O in less than 12 hours at 140°C. There is evidence that the material used is not pure AgO but may contain water, some higher oxide of silver, or both. Further experiments should indicate which it is.

Electrochemically-prepared AgO is also impure, containing either water or a higher oxide of silver. Initially, the material appears to be in some relatively unstable form either as a chemical species or a crystal form. This characteristic requires further investigation.

Proposed Work

The thermal balance is to be further modified to allow long-term constant-temperature runs. Constant-temperature thermograms of electrolytic AgO will be made and further constant-temperature thermograms of chemical AgO will be prapared at temperatures other than 140°C. An attempt will be made to isolate the impurity in these materials.

Commericial AgO will be investigated if it can be found in a reasonably pure form. Varying-temperature thermograms will be made at lower heating rates.

Table 1

Precipitation of ZnO with KOH

Expt Number	Temp (°C)	Number of Washings	A in last Washing (cmp/50λ)	Zn(II) Recovered (meq)	Apparent % $Zn(OH)_2$	Remarks
1	55	6	19	100	11.1	Zn(II) soln. added to KOH soln.
2	"	"	28	100	18.0	
3	"	"	99	98	21.9	
4	25	10	0	94.5	1.4	KOH soln. added to Zn(II) soln.
5	"	"	27	92.5	21.8	
6	25	11	6	100	0.7	KOH soln. added to Zn(II) soln.
7	"	"	49	96.3	8.9	
8	"	"	38	95.0	13.8	
9	--	5	--	92.0	14.3	KOH soln. added to Zn(II) soln. Wash water contained tritium.
10	--	"	--	92.5	19.9	Washing by centrifuge method. No temp. control.
11	--	"	--	94.5	19.6	

Table 2

Precipitation of $Zn(OH)_2$ with NH_3

Expt Number	Temp (°C)	Number of Washings	A in last Washing (cmp/50λ)	Zn(II) Recovered (meq)	Apparent % $Zn(OH)_2$	Remarks
1	25	6	192	72.5	37.1	Zn(II) soln. added to NH_3 soln.
2	"	"	115	55.0	7.5	
3	"	"	154	75.0	29.8	
4	55	11	12	81.6	(101)	NH_3 soln. added to Zn(II) soln.
5	"	"	31	87.5	96.2	
6	"	"	18	84.5	97.3	
7	--	12	205	80.0	1.2	Zn(II) soln. added to NH_3 soln. Washed by centrifuge method.
8	--	"	264	80.0	17.5	No temp. control
9	--	"	208	82.5	12.1	
10	--	9	--	95.7	83.0	Zn(II) soln. added to NH_3 soln. Wash water contained tritium.
11	--	"	--	91.6	90.2	Washed by centrifuge method. No temp. control.
12	--	"	--	90.0	99.3	

Table 3

Precipitation of Cadmium with KOH and NH_3

Expt Number	Temp (^{o}C)	Number of Washings	A in last Washing (cmp/50λ)	Cd(II) Recovered (meq)	Apparent % $Cd(OH)_2$	Remarks
1	25	11	27	88.8	40.4	Cd(II) soln. added to KOH soln.
2	"	"	30	87.5	34.3	
3	"	"	23	86.3	45.2	
4	25	9	18	25.0	16.9	Cd(II) soln. added to NH_3 soln.
5	"	"	13	30.4	42.1	
6	"	"	22	26.3	14.7	

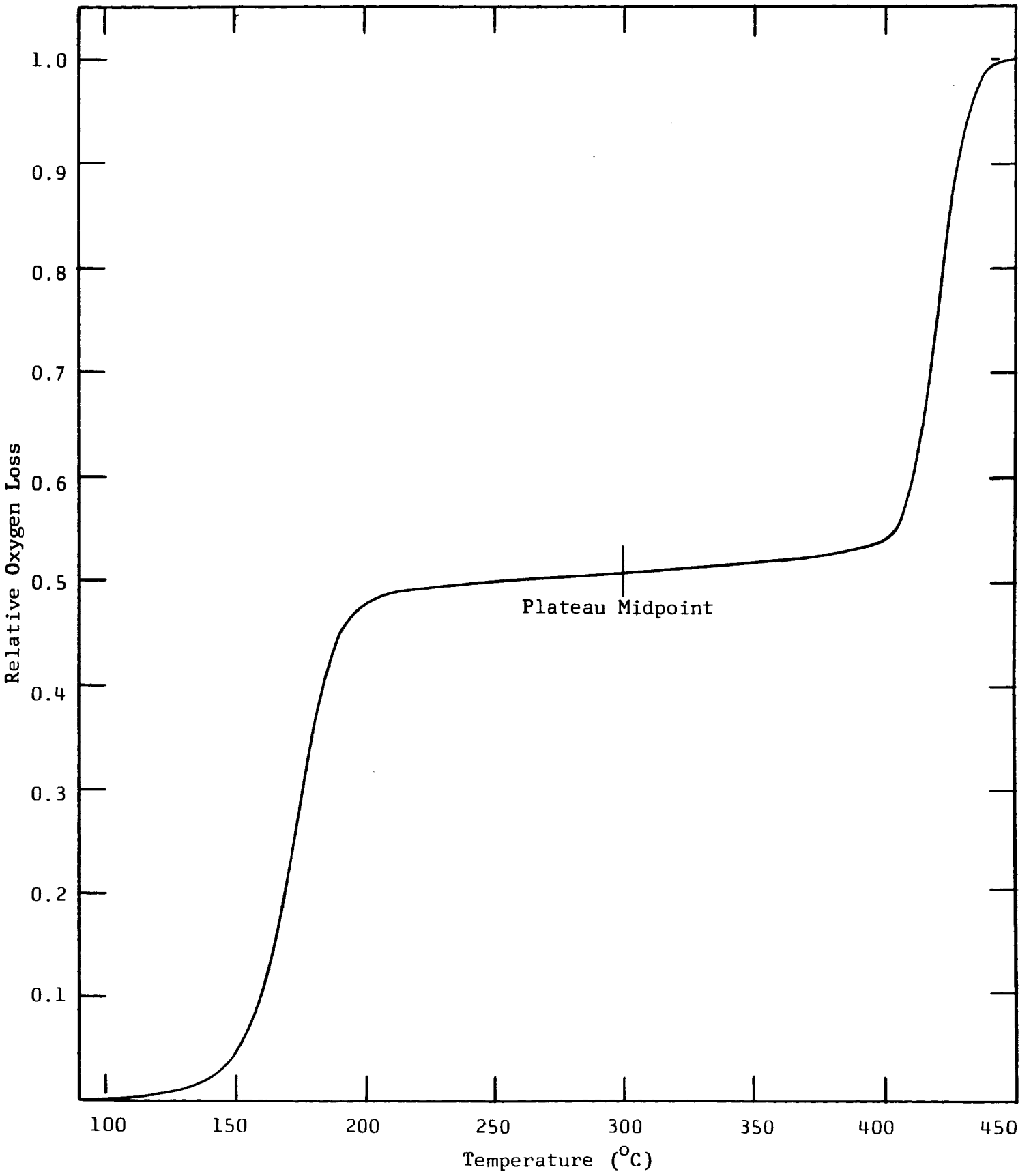

Figure 1. Thermogram of Ag_2O at ΔT Rate of 5°/Minute

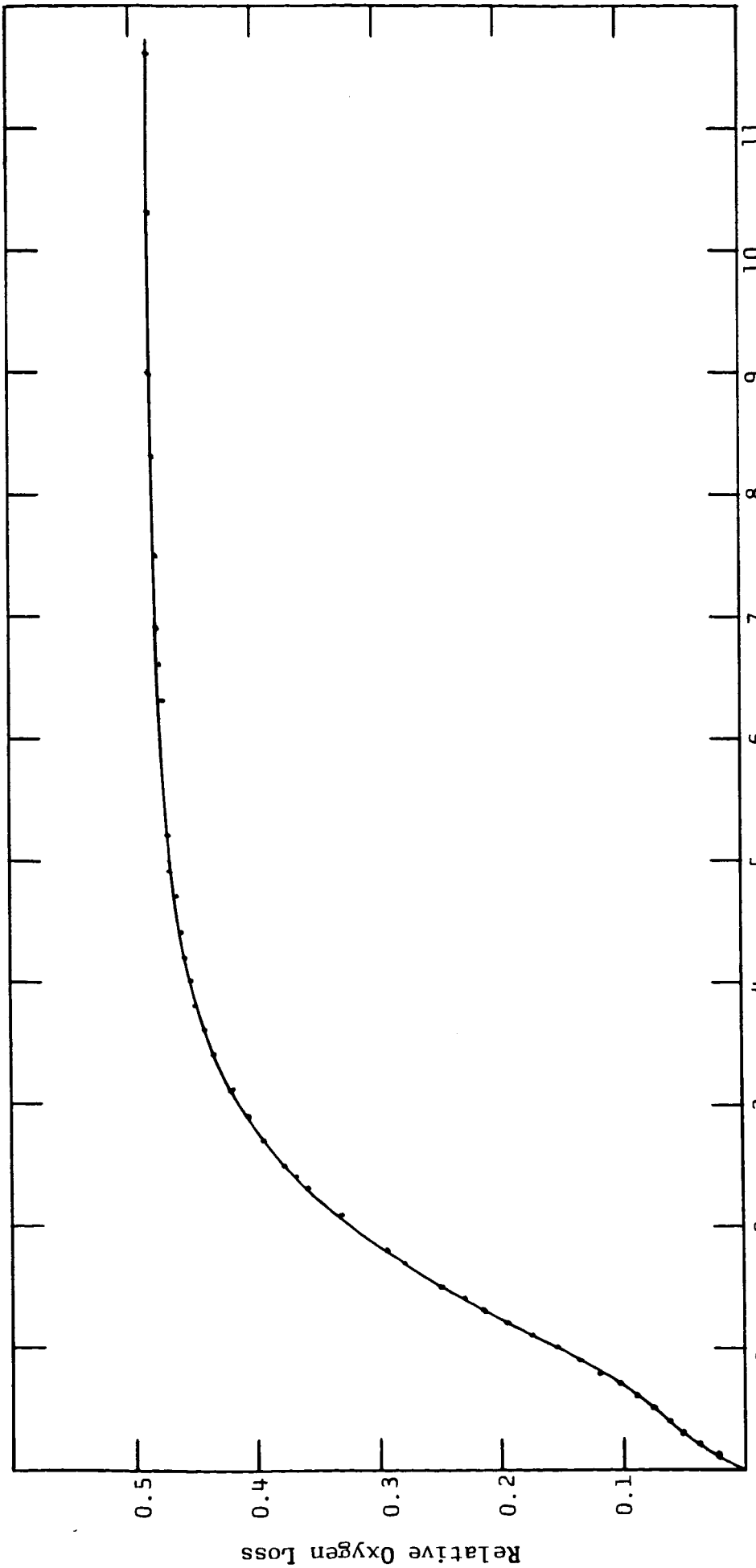

Figure 2. Constant-Temperature Thermogram at 140°

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